Photochemical Cyclization of the Phenalenyl Carbanion. The Role of Benzophenone

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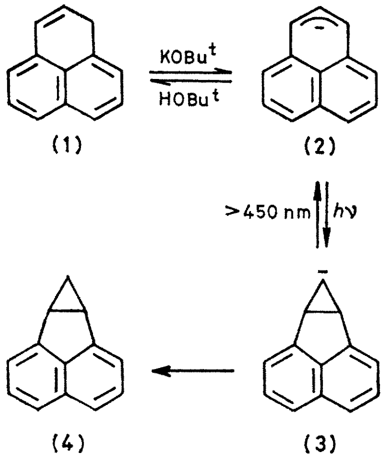
Summary The photocyclization, using visible light, of the phenalenyl anion (**2**) proceeds in near quantitative yield when benzophenone is added.

In recent years there has been a renaissance of interest in the photochemistry of carbanions but with intermittent successes.[1] Our interest in carbanion electrocyclization reactions prompted us to look at light-induced pathways to ring-closure reactions of delocalized carbanions. One reason why the phenalenyl anion (**2**) was selected was that, in accord with orbital symmetry, the cyclopropa-acenaphthenyl anion (**3**) opens reluctantly.[2] We chose to run the photochemical reaction in t-butyl alcohol–potassium t-butoxide at room temperature because under these conditions phenalene (**1**)[3] is partly converted into (**2**) (*ca.* 0·5% in 0·15 M-$KOBu^t$) but more basic anions [*e.g.* (**3**)] would be quickly protonated.



As indicated in run 1 of the Table, irradiation (>450 nm) (Hanovia 450-W Hg lamp with a Corning 3387 yellow filter) of the long wavelength bands due to (**2**) (λ_{max} 530, 480 nm) led to complete loss of (**1**) with the production of a copious white but air-sensitive polymeric precipitate (m.s., n.m.r. spectroscopy, and $\bar{M}_n$ by vapour pressure osmometry). There were no detectable monomeric products. However when the concentration of (**1**) was reduced (run 2), the amount of polymeric material was also reduced and cyclopropa-acenaphthene (**4**)[2,4] was obtained in 30% yield.

A consideration of possible mechanistic pathways led us to investigate the role electron-transfer agents might play. Among the substances which augmented the yield of (**4**), benzophenone proved to be most effective (runs 3—7) and led to near quantitative conversion of (**1**) into (**4**) (runs 4 and 6). As is indicated by the results of run 5, and was confirmed by monitoring the progress of the reaction (h.p.l.c.), increasing the concentration of benzophenone also had the effect of reducing the rate of disappearance of (**1**). There is no evidence for loss of benzophenone in these reactions and its role is to suppress polymerization rather than accelerate cyclization. If the substrate concentration becomes too large even in the presence of benzophenone (runs 6 and 7) polymerization can become important.

In view of the demonstrated photostability of (**1**) and (**4**) at the wavelengths used and the high triplet energy of benzophenone,[5] a photoexcited anion(s) of (**2**) is clearly involved. It would appear that electron transfer, leading to polymerization, is competitive with cyclization of photoexcited (**2**) be it *via* a singlet or triplet in an electrocyclic, di-π-methane, or more complex process.

Table. Photoreactions of phenalene in 0·15 M $KOBu^t$–$HOBu^t$.[a]

				Products[b]		
Run	Substrate conc./M	Benzophenone conc./M	Time/h	% (**1**)	% (**4**)	Polymer
1	0·082	—	22	<5	<5	ppt.
2	0·012	—	5·5	1	30	ppt.[c]
3	0·012	0·004	21	2	78	no ppt.
4	0·012	0·012	21	2	92	slight ppt.
5	0·012	0·046	75	68	20	no ppt.
6	0·023	0·012	46	—	101	no ppt.
7	0·046	0·0095[d]	34	14	53	—

[a] In runs 1 and 7, base conc. = 0·13 *J*. [b] Reaction followed by reversed-phase h.p.l.c. calibrated with an internal standard. [c] $\bar{M}_n$ = 805 by vapour-pressure osmometry. [d] No loss of benzophenone during reaction.

While this is not the first example of photochemical carbanion cyclization to form a three-membered ring,[6] it has proceeded in high yields and suggests a potential role for electron transfer agents.

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